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CONCENTRATION OF BROMIDE IONS IN
SEAWATER BY ISOTOPIC EXCHANGE

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A study was conducted to determine the feasibility of concentrating radioactive bromide ions in seawater by passing the seawater through a column of silver bromide. The radioactive bromide ions in the seawater are isotopically exchanged with the bromide ions in the silver bromide. The effect of column height, flow-rate, volume and/or residence time of seawater on the amount of bromine exchanged was studied and each of these variables was found to have a significant effect.

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Concentration of Bromide Ions in Seawater by Isotopic Exchange

There is a need for determining radioactive bromide ions in the ocean. The amount of bromine in seawater is relatively small (65 mg/l), and a substantial improvement in detection sensitivity could be achieved by concentration of the bromine. Required is a fast-reacting, in situ system for concentration capable of accomodating large volumes of seawater.

A preliminary study has been made of isotopic exchange as a possible method for concentrating bromine in seawater. Silver bromide has been used with success in retaining bromide ions from seawater at high flow rates, for large volumes of seawater, and for sufficient lengths of time to permit counting of any radioactive bromine atoms present.

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ROBERT WILLIAMSON II
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

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INTRODUCTION

A method is required for the in-situ determination of radioactive bromide ions in the ocean. The amount of radioactive bromide ions is expected to be very low and thus sensitive methods of analysis are sought. Several investigators have made low-level determinations of other radionuclides in seawater (1-4) by means of in-situ gamma-ray probes coupled to counters or to pulse-height spectrometers. A substantial improvement in sensitivity could be achieved if the radioactive bromide ions in the seawater were to be concentrated and then counted.

BACKGROUND

Commonly used methods of concentration of radionuclides in seawater are: (1) co-crystallization(5), (2) evaporation or freeze drying(6), (3) co-precipitation(7), (4) solvent extraction(8), (5) ion-exchange(9) and (6) isotopic exchange(10,11). Of these several methods isotopic exchange appears to be the most appropriate for the present application where a fast-reacting, in-situ system is required and large quantities of seawater are involved.

In the isotopic exchange method, as applied to this problem, seawater would be passed through a porous bed containing bromide ions bound into a crystal lattice. Bromide ions in the seawater would exchange with the bromide ions in the bed. In the isotopic exchange process, there appears to be an initial rapid exchange in which the exchanged ion is either retained for a short period and then released by subsequent exchange or retained semi-permanently. Exchange takes place at the surface of the crystal lattice, and the new ion may get buried deep within the lattice as a result of diffusion and/or recrystallization. Koltoff (10) concluded from his studies that recrystallization was the principal mechanism involved in such retention, and Polessitisky (11) and co-workers estimated that the self-diffusion coefficient of Br^- in a silver bromide (AgBr) bed is at least one thousand times too small to account for observed rates of the AgBr - Br^- exchange reaction.

APPROACH

Seawater samples containing [82]Br were passed through an isotopic exchange bed of AgBr. The amount of [82]Br exchanged was determined by gamma counting aliquots of the seawater samples before and after passage through the AgBr column.

A 3 x 3 factorial experiment was set up to study the effect of several variables (factors) on the amount of [82]Br exchanged. The factorial experiment is useful in determining whether or not

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variations due to factors studied are greater than might be expected from purely random variations, and also in determining whether or not interactions between pairs of factors are significant. The factors studied in this experiment were the following: (1) height of the AgBr column, (2) flow-rate, and (3) residence time (i.e., time duration of flow).

In addition to the factorial experiment, the desorption rate of ^{82}Br from the AgBr column was studied.

EXPERIMENTAL

MATERIALS

1. Silver bromide (Fischer and Baker). The silver bromide was crushed and sieved through a Tyler standard screen. A 12-24 mesh screen (701-1397 microns) was used.

2. Synthetic seawater. Synthetic seawater is made by dissolving simulated sea salt mix, (Lake Product Co. Inc., St. Louis, Mo.) in distilled water. Simulated sea salt mix contains those elements found in natural sea salt in quantities greater than 0.004%.

3. Radioactive bromine. ^{82}Br was obtained by thermal neutron activation of ammonium bromide. A stock solution was made by dissolving the irradiated ammonium bromide in distilled water. An aliquot of the stock solution was added to synthetic sea water and stored in a polyethylene bottle.

APPARATUS

1. Exchange columns. Three columns were made, each consisting of a Pyrex tube (0.77 cm i.d.) with a glass frit on the bottom. The columns were each loaded with a water slurry of AgBr. Column 1 was filled to a height of 1 cm, Column 2 to a height of 3 cm, and Column 3 to a height of 9 cm. The dry weight of AgBr used for each column was 1, 3 and 9 g, respectively.

2. Vacuum pump. A Duo Seal pump was used to draw the seawater through the column into a suction flask attached to the bottom of the column.

3. Vacuum gage. In order to obtain reproducible flow rates, a gage which measures the vacuum in inches of mercury was used. Vacuum was adjusted by bleeding air into the system through a stopcock (see Figure 1).

4. Gamma-ray counter. A sodium iodide [NaI(Tl)] scintillation detector with a well was used. The NaI(Tl) crystal was 3 in. dia. x 3 in. long, and was encased in a lead shield 3 in. thick.

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PROCEDURE

Seawater was passed through the isotopic exchange columns at various flow rates. The fraction of the radioactive bromide ions retained on a column was determined by counting an aliquot of the stock synthetic seawater and a similar aliquot of the seawater that had been passed through the column and comparing the two counts.

A series of runs were made on each of the three columns in accordance with the flow-rates and residence times shown in Table 1. The corresponding volume of seawater used in each run is also shown in Table 1.

The rate of desorption of ^{82}Br from AgBr was also studied. For this study, a 9 cm and a 1 cm column, each containing ^{82}Br, were each washed with four 10 ml aliquots of seawater which did not contain ^{82}Br. For these washings, flow rates of 3.73 and 9.07 $ml/cm^2/sec$ were used for the 9 cm and the 1 cm columns, respectively. The washes were made in rapid succession.

The apparatus used for these measurements is shown in Figure 1.

RESULTS

The data obtained are shown in Table 1 and the results of the data analysis are shown in Table 2. A description of the statistical treatment of the data obtained in a factorial experiment such as this may be found in standard texts on experimental statistics. The F ratios in Table 2 are the ratios of the "mean square" of a factor (e.g., volume, flow-rate, or amount of AgBr) to the "mean square" of the error. Rather than determine the random error by replication, the error term was determined from the second-order interactions between the three factors. By comparing the F ratios in Table 2 with those tabulated by Fisher and Yates (12) for tests of significance, it is seen that, in the ranges studied, the amount of AgBr, flow-rate, residence time as well as the interactions between these factors all have significant effects on the isotopic exchange of ^{82}Br with AgBr.

The observations in Table 1 are also presented in plotted form in Figure 2. From Figure 2, it can be readily seen that the isotopic exchange of ^{82}Br with AgBr increases with column height, decreases with flow rate, and, to a lesser extent, decreases with residence time.

The data obtained in the desorption study are presented in Table 3. Initially, the radioactive bromide ions are rapidly desorbed, but the rate of desorption diminishes with time.

CONCLUSION

The results obtained indicate that bromide ions in seawater can be concentrated by the technique of isotopic exchange. The AgBr can

concentrate the bromide ions in seawater and the seawater can desorb
the bromide ions from the AgBr. Optimization of the concentration
system would involve trade-offs between column size, flow-rate and
counting procedure. Retention factors of even 20-30% would result
in a reduction of detector size required by a factor of approximately
5×10^3, provided suitable flow-rates through the exchange bed can
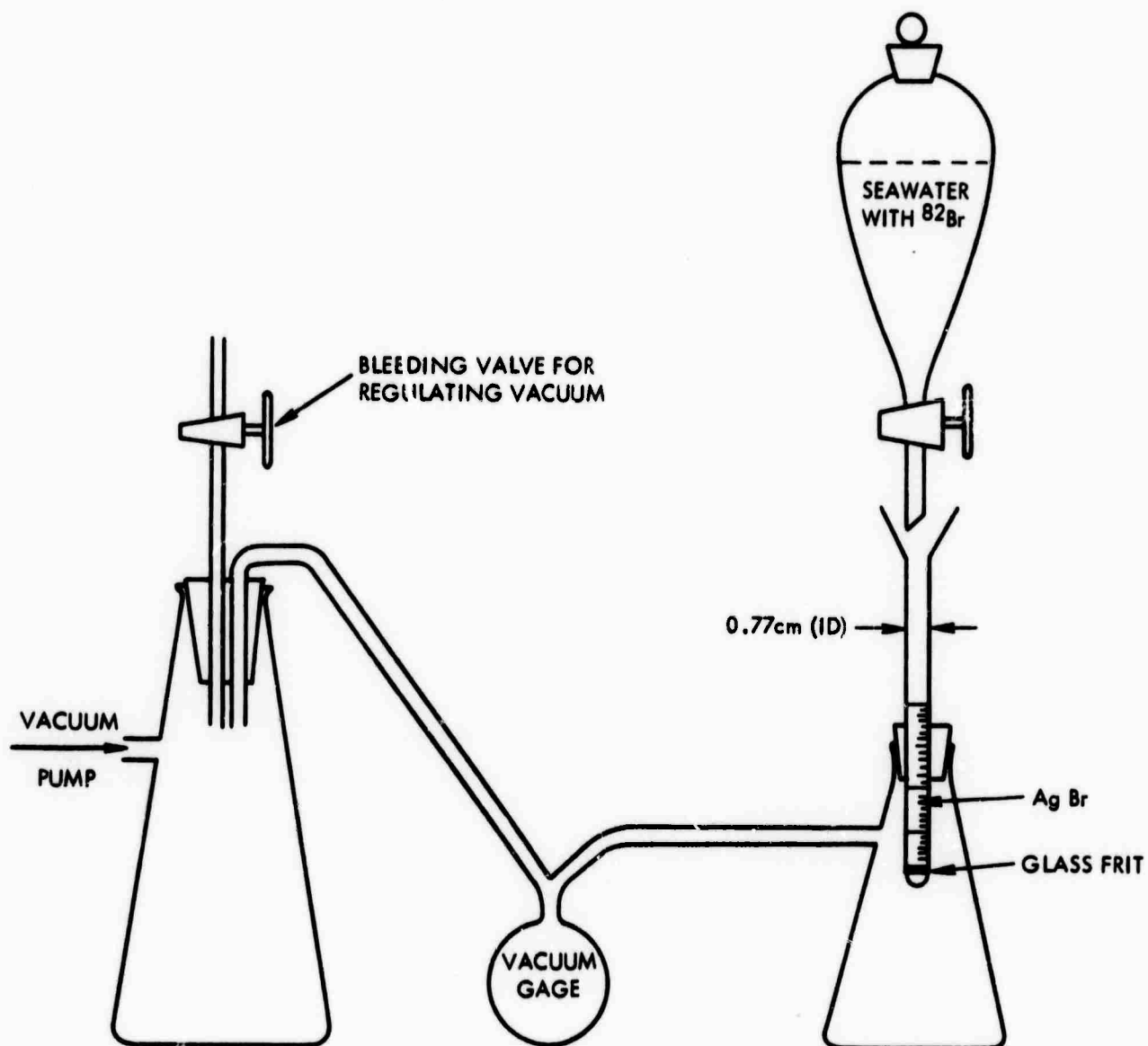be achieved, and that the desorption time is not excessive.

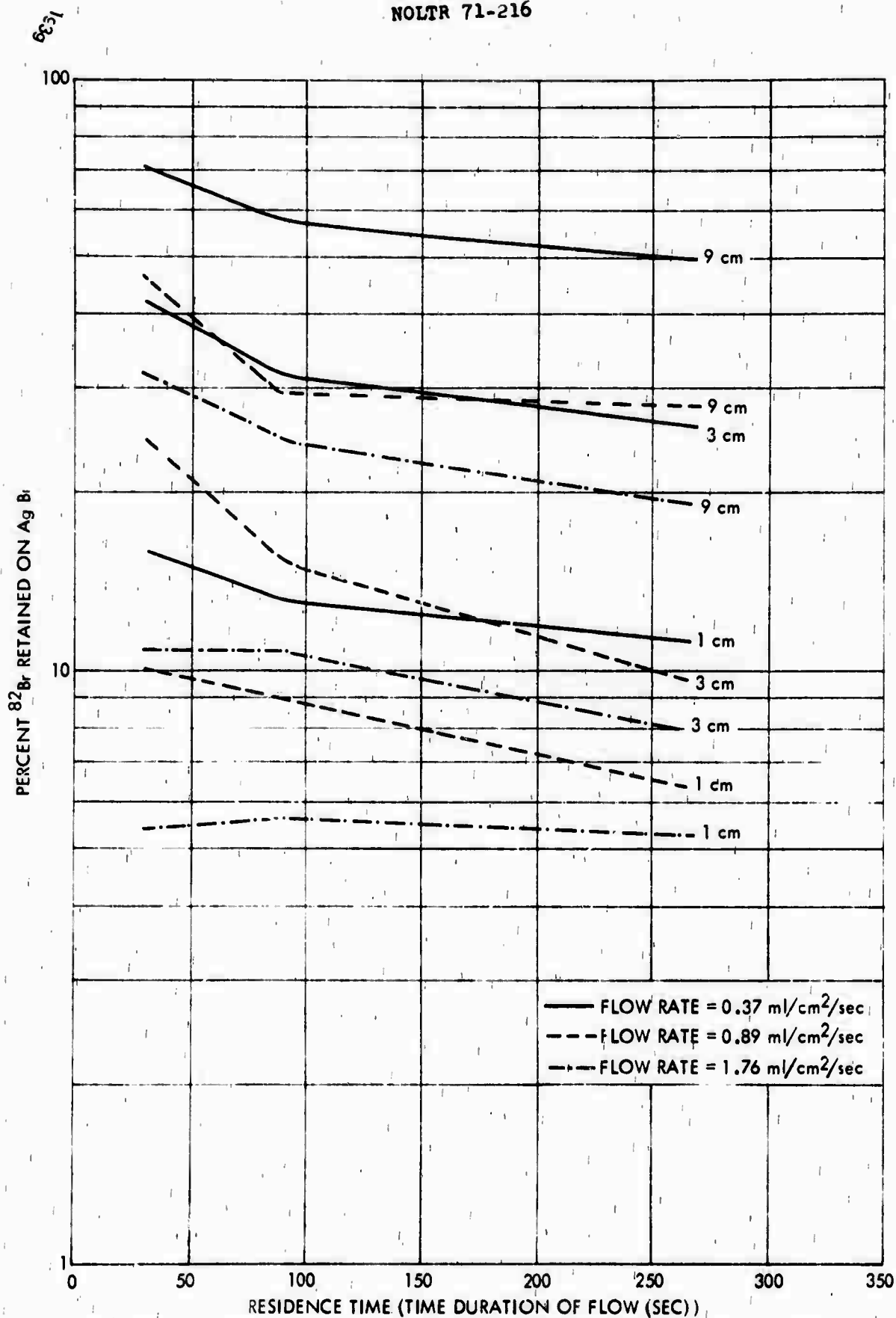FIG. 1 APPARATUS USED FOR THE ISOTOPIC EXCHANGE

FIG. 2 RETENTION OF BROMIDE IONS IN SEAWATER BY ISOTOPIC EXCHANGE IN Ag Br COLUMNS

TABLE 1

ISOTOPIC RETENTION OF ^{82}BR WITH SILVER BROMIDE

Volume (ml)	Residence time (sec)	Bromine Retention (%)		
		Col. 1 (1cm)	Col. 2 (3cm)	Col. 3 (9cm)
Flow-rate = 0.37 ml/cm^2/sec				
5	30	16.0	42.4	70.3
15	90	13.2	31.4	57.9
48	270	11.2	26.0	50.3
Flow-rate = 0.89 ml/cm^2/sec				
13	30	10.1	24.9	46.2
39	90	9.3	15.4	29.3
115	270	6.4	9.6	28.2
Flow-rate = 1.76 ml/cm^2/sec				
25	30	5.4	10.8	31.8
75	90	5.6	10.7	24.7
245	270	5.3	8.0	19.3

TABLE 2

STATISTICAL ANALYSIS OF THE DATA

Factors	Degrees of freedom	Sum of squares of deviations	Mean squares	F ratios
Single Factors				
Volume	2	519	259	61.7
Flow rate	2	2293	1146	272.8
AgBr	2	4360	2180	519.0
Interactions				
Volume x Flow Rate	4	77	19	4.5
Volume x AgBr	4	166	42	9.9
Rate x AgBr	4	569	142	33.9
Volume x Flow Rate x AgBr	8	34	4.2	
(error)				

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TABLE 3

DESORPTION OF ^{82}BR FROM AgBr

Seawater Washes	^{82}Br desorption (%)	
(10 ml aliquots)	(9g)	(1g)
First	27.2	56.7
Second	8.1	5.7
Third	2.1	1.4
Fourth	0.9	0.7

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